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Enhanced decomposition of dimethyl phthalate via molecular oxygen activated by Fe@Fe_2O_3/AC under microwave irradiation

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HIGHLIGHTS

- Microwave irradiation induces the electrons transferring from AC to Fe@Fe_2O_3 and reacts with molecular oxygen.
- Microwave heating accelerates the electron transferring from AC to Fe@Fe_2O_3 to generate reactive oxygen species.
- This environmental remediation method is feasible for aqueous organic pollutants treatment.

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ABSTRACT

In this study, we demonstrate that the decomposition of dimethyl phthalate under microwave irradiation could be greatly enhanced over Fe@Fe_2O_3 nanowires supported on activated carbon (Fe@Fe_2O_3/AC). The great enhanced decomposition of dimethyl phthalate could be attributed to a unique microwave induced molecular oxygen activation process. Upon microwave irradiation, electrons could be transferred from activated carbon to zero-valent iron, and then react with molecular oxygen to form $O_2^{\bullet-}$ and $^{\bullet}OH$ radicals for the decomposition of dimethyl phthalate. The deactivation and the regeneration of Fe@Fe_2O_3/AC catalyst were systematically studied. We also found that microwave heating could accelerate the electron transferring from AC to Fe@Fe_2O_3 to generate more reactive oxygen species for the decomposition of DMP than conventional oil bath heating. This novel molecular oxygen activation approach may find applications for wastewater treatment and drinking water purification.

1. Introduction

The plasticizer scandal attracts people's attention on food security and plasticizer abuse. As a representative of industrial plasticizers, dimethyl phthalate (DMP) has been widely used as the additive in cosmetics, varnishes, insecticide and cellulose acetate film to improve the flexibility. It could easily leach into the atmosphere, water and soil during its production and application [1–3]. The accumulation of DMP in human and animals would result in potential health hazard and endocrine-disrupting effects [4,5]. DMP is rather stable in the environment and difficult to be naturally degraded with biological and photo-chemical methods [6–8]. Therefore, many scientists seek for advanced oxidation methods to decompose DMP to less toxic substance. For instance, Liu et al. [9] developed an electro-Fenton process with an in situ reaction-controlled pH adjustment function to degrade DMP. They found that this electro-Fenton process could effectively decrease the concentrations of DMP and the total organic carbon in 60 min. Chen et al. investigated the photocatalytic degradation of DMP over titanium dioxide-coated magnetic poly(methyl methacrylate) (TiO_2/mPMMA) and platinum-doped TiO_2/mPMMA microspheres and found these photocatalysts possessed high photocatalytic activity, magnetic separability and good durability during the DMP degradation [10]. Xu et al. [11] revealed that DMP could quickly and nonselectively be decomposed by hydroxyl radicals generated during the UV photolysis of hydrogen peroxide. Li et al. [12] utilized CeO_2 supported on activated carbon to catalytic ozonation of DMP, and also studied photocatalytic ozonation of DMP on TiO_2 prepared by a hydrothermal method at a low temperature [13]. Obviously, these reported methods for DMP degradation required the utilization of additional electricity or light or expensive oxidants like H_2O_2 and ozone.

Elimination of toxic organic pollutants in water by oxidation with molecular oxygen is one of the most environmentally friendly pollution-treatment methods [14]. However, ground-state molecular oxygen is not active enough for organic compound oxidation at ambient condition because of spin restrictions. Thus the activation of molecular oxygen for environmental remediation has received increasing attention in recent years. The activation of molecular oxygen could generate reactive oxygen species ($O_2^{\bullet-}$ and $^{\bullet}OH$) to decompose organic contaminant [15]. It is well known that hemoproteins in biological systems and dinuclear iron centers in

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proteins could activate molecular oxygen in metabolic reactions [16]. Inspired by this biological molecular oxygen activation process, Gosling and Nolte [17] utilized a rhodium (III) bipyridine complex and manganese (III) porphyrin to activate molecular oxygen for the epoxidation of alkenes. Rutkowska-Zbik and Witko [18] reported the modeling of the activation of molecular oxygen by the five-coordinate manganese (III) porphyrin and the subsequent hydrogen adsorption processes formed the reactive manganese (V) oxo complex. Zhao and co-workers [14] revealed that FeBR, an iron (II) complex of 2, 2′-bipyridine supported on a commercial cationic ion exchange resin could activate molecular oxygen at room temperature to degrade organic pollutants including rhodamine B, malachite green, and N,N-dimethylaniline in aerated aqueous solutions under visible-light irradiation ($\lambda > 420$ nm), which was a simple and green heterogeneous photocatalytic molecular oxygen activation approach to degrade organic pollutants. Bonchio et al. [19,20] found that $[\mathrm{Ru^{II}(DMSO)PW_{11}O_{39}}]^{5-}$ polyoxotungstates could catalyze the oxidation of DMSO to $DMSO_2$ in water and iron-substituted polyoxotungstates could catalyze cyclohexane oxygenation with molecular oxygen under microwave (MW) irradiation.

Recently, our group developed a rapid catalytic MW method to deal with *Microcystis aeruginosa* by $FeCl_3$-loaded active carbon ($FeCl_3$/AC) [21]. We attributed the catalytic induced *M. aeruginosa* damage under MW irradiation to the charge transfer-induced doping effect. When $FeCl_3$/AC was added into *M. aeruginosa* suspension, the cells could quickly be adsorbed on the surface of AC. The so-called charge transfer-induced doping effect could then realize electrons transferring from AC to Fe^{3+} ions, thus leaving holes on AC to attack and oxidize the cells. If we replace $FeCl_3$ with some electron sinks, the electrons transferring from AC would not be trapped by Fe^{3+} ions, but possibly further transfer to molecular oxygen via the interchange of the electron sinks. This idea might be a novel molecular oxygen activation approach. Motivated by this idea, in this study we deposit Fe@Fe_2O_3 nanowires on AC by reducing iron ions absorbed on AC with sodium borohydride to utilize Fe@Fe_2O_3 nanowires as an electron sink. As expected, we find the resulting Fe@Fe_2O_3 nanowires loaded on AC (Fe@Fe_2O_3/AC) could greatly enhance the decomposition of DMP under MW irradiation. The reasons for the great enhancement of DMP degradation are analyzed in detail.

2. Materials and methods

2.1. Materials

The dimethyl phthalate (99%) was obtained from Sigma–Aldrich (St. Louis, MO, USA). Sodium borohydride (96%), iron (III) chloride hexahydrate (99%) and molecular sieve (MS) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Acetonitrile (HPLC grade) was purchased from Tedia Company, Inc. (U.S.A.). Activated carbon was obtained from GongYi Taihe wastewater treatment material Co. Ltd., China. All solutions were prepared in de-ionized water.

2.2. Preparation of the Fe@Fe_2O_3/AC catalyst

The Fe@Fe_2O_3/AC catalyst was prepared by the reduction of iron ions absorbed on AC with sodium borohydride aqueous solution with a similar procedure for the synthesis of Fe@Fe_2O_3 core–shell nanowires [22]. Coal-based columnar activated carbon was washed with de-ionized water for several times and then immersed in 8–10 wt% hydrochloric acid for 18 h. The acid treated activated carbon was then treated with boiling water for 2 h and washed with de-ionized water until the pH reached 5–6. Finally, the pretreated AC was dried in an oven at 105 °C for 8 h for use [21–24]. For the loading of Fe@Fe_2O_3 core–shell nanowires, the pretreated AC was first soaked in ferric chloride solution ($FeCl_3$, 0.1 M) under stirring for 3 h for ferric iron absorption. The soaked AC was then washed with deionized water to remove unabsorbed $FeCl_3$ on the surface of AC and reacted with 1 M of sodium borohydride solution added dropwise for the deposition of Fe@Fe_2O_3 on AC at an ambient temperature. The resulting Fe@Fe_2O_3/AC sample was washed with de-ionized water several times and dried under nitrogen flow. The content of Fe@Fe_2O_3 loaded on AC was found to be ca. 1.4 wt% according to atomic absorption spectroscopy analysis. For comparison, the Fe@Fe_2O_3 supported on molecular sieve (Fe@Fe_2O_3/MS) catalyst was prepared by the similar method with Fe@Fe_2O_3/AC. The $FeCl_3$/AC catalyst was obtained without the reduction of ferric ions with sodium borohydride solution [21]. The Cu supported on activated carbon (Cu/AC) catalyst was prepared with the similar method by using $CuCl_2$ solution instead of $FeCl_3$ solution. The Fe_2O_3/AC catalyst was prepared by wetness impregnation of AC with iron nitrate solution followed with a subsequent calcination [25].

2.3. Experimental procedure

The degradation experiments were performed in a round flask in a 400 W temperature-controllable MW oven (MAS-1, Shanghai Xinyi Ltd. China) (Fig. 1). As shown in Fig. 1, in order to prevent volatilization of the solution, a condenser was mounted on the round flask. At the beginning, 50 mL of DMP (11.9 mg/L) aqueous solution and 1 g of different catalysts were added into a 100 mL round flask. Then set up the parameters

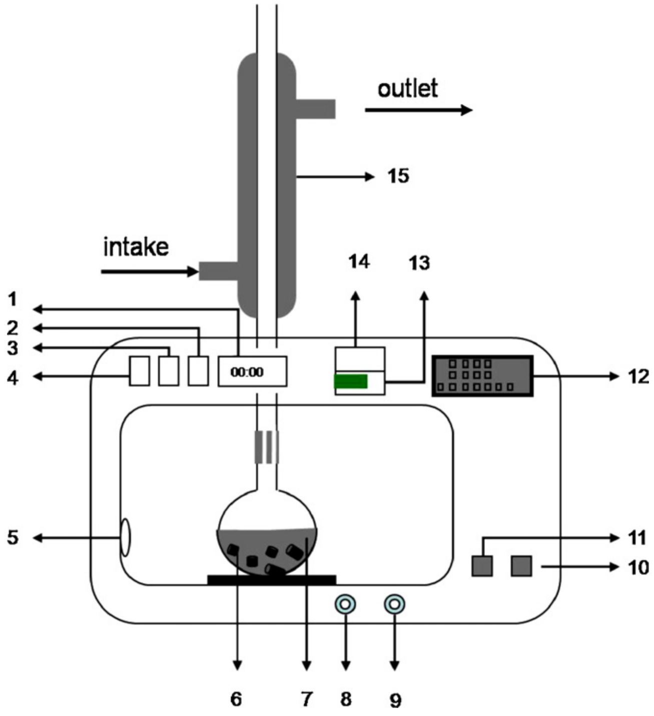

Fig. 1. Schematic illustration of experimental apparatus: (1) time display; (2) temperature display; (3) process step display; (4) scheme (5) temperature sonde; (6) Fe/AC catalysts; (7) reaction solution; (8) stirrer type adjuster; (9) rotate speed adjuster; (10) start button; (11) open button; (12) adjuster buttons; (13) power display; (14) rotate speed display; (15) condenser.